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anhydrous AlCl$_3$ (0.5 g, 3.8 mmol) was added. The solution which stirred overnight at 0 °C turned wine red. The CH$_2$Cl$_2$ solution was extracted with cold water; removal of solvent gave **6**, an oil: ^{1}H NMR δ 0.98 (d, 3 H, J = 6 Hz), 1.29 (s, 3 H), 1.35 (s, 3 H), 2.0 (m, 1 H), 2.70 (dd, 1 H, J_{AB} = 6 Hz, J_{AC} = 14 Hz), 3.35 (dd, 1 H, J_{BA} = 5 Hz, J_{BC} = 14 Hz), 6.96–7.59 (m, 4 H).

Reaction of AgF with Benzenesulfenyl Chloride. To 0.88 g of AgF (6.9 mmol) in acetonitrile (4.0 mL) under nitrogen was added 1.00 g of benzenesulfenyl chloride (6.9 mmol) with stirring. A precipitate formed, and the solution turned canary yellow. After 1 h, the solution was almost colorless. Silver chloride (0.81 g, 82%) was recovered by filtration. ^{19}F NMR of the remaining solution showed a multiplet at δ −173. On attempted distillation the signal disappeared. Diphenyl disulfide (0.73 g, 95%) was recovered after removal of solvent.

Acknowledgment. We thank Dan Woodard for technical assistance.

Registry No. **3**, 57187-86-7; **6**, 54442-00-1; **8**, 100655-83-2; **9**, 84538-93-2; **10**, 36219-91-7; AgF, 7775-41-9; HgF$_2$, 7783-39-3; FCH$_2$CH(SPh)CH$_2$Cl, 100655-81-0; CH$_3$(CH$_2$)$_7$CH(F)CH$_2$SPh, 100655-82-1; (CH$_3$)$_3$CCH(SPh)CH$_2$F, 100655-76-3; HO(CH$_2$)$_2$CH(SPh)CH$_2$F, 100655-77-4; CH$_3$(CH$_2$)$_7$CH(SPh)CH$_2$F, 100655-78-5; PhCF(CH$_3$)CH$_2$SPh, 100655-79-6; (CH$_3$)$_3$CCH=CH$_2$, 558-37-2; HOC(CH$_3$)$_2$CH=CH$_2$, 115-18-4; CH$_3$(CH$_2$)$_7$CH=CH$_2$, 872-05-9; PhC(CH$_3$)=CH$_2$, 98-83-9; CH$_2$=CHCH$_2$Cl, 107-05-1; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; benzenesulfenyl chloride, 931-59-9; diphenyl disulfide, 882-33-7; 1-(phenylthio)-2-fluorocyclohexane, 97231-52-2; 2-methyl-2-fluoro-1-(phenylthio)cyclohexane, 100655-80-9.

Preparations and Reactions of 10-(Halomethylene)anthrones

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(Halomethylene)anthrones **3** and **4** were prepared by the simple method from 10-methylene- and 10-benzylideneanthrones. The reaction of **3** with azide ion gave 10-(azidomethylene)anthrone **5a**, which afforded **16** and/or **17** by photolysis and thermolysis, while similar treatment of **4** led to spiro[anthroneazirine] **19**. The reaction of **3** and **4** with cyanide ion gave the corresponding 10-(cyanomethylene)anthrones **5b** and **6b**. (Halomethylene)anthrone **3** reacted with methoxide ion, hydroxide ion, and aniline to give **5c**, **5d**, and **5e**, respectively.

Methyleneanthrones are members of a class of compounds which are called "quinone methides", that is, compounds in which one carbonyl oxygen atom of a quinone is replaced by a methylene (or substituted methylene) group. This system is unstable and is subject to ionic addition and cycloaddition reactions because of the strong driving force for reaction supplied by aromatization of the product.[1] However, 10-methyleneanthrones, e.g., **1** and **2**, are stable and show no tendency toward spontaneous aromatization. The low probability of the central ring becoming aromatic makes their quinone methide character weak. Since the ethylenic bond is comparatively isolated from the carbonyl group in the molecule, these compounds behave as a quinone methide as well as an olefin.[1]

The chemistry of methyleneanthrones having an unsubstituted and aryl-substituted exomethylene group has been widely studied. They are useful starting or intermediate materials for a number of syntheses including the preparation of fused polycyclic compounds,[1a,c] 9,10-disubstituted anthracenes whose substituents are functionalized,[1a,2] and spiroanthronyl-substituted compounds which contain an anthrone (quinonoid) moiety and a carbocycle or heterocycle in spiroconfiguration.[2b–f,3] On the other hand, methyleneanthrones whose exomethylene is substituted by a group other than an aryl have received less attention, though some of their unique properties were known as described below. 10-(Hydroxymethylene)anthrone, prepared by the treatment of spiro[anthrone-10,2′-oxirane] with boron trifluoride etherate, is in tautomeric equilibrium in solution with 10-formylanthrone and 10-formyl-9-hydroxyanthracene. Also it has been converted into α-chloro-, α-methoxy-, and α-benzoyloxy-substituted methyleneanthrones.[2b–d] The solvolysis reaction via intermediate vinyl cations of 10-(α-bromoarylidene)anthrones, which are prepared by dehydrobromination of 10-arylideneanthrone dibromides, has been studied.[4] The present paper is concerned with the syntheses and reactions of α-substituted 10-methylene-

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Table I. Reactions of the (Halomethylene)anthrones 3 and 4 with Nucleophiles

	reaction conditions					
compd	nucleophile	solv	temp, °C	time, h	product	yield, %
3a	N_3^-	DMF	0	0.5	**5a**	94
3b	N_3^-	DMF	0	0.5	**5a**	92
4b	N_3^-	DMF	20	0.5	**19**	90
3a	CN^-	95% DMF	20	0.5	**5b**	20
3b	CN^-	95% DMF	20	0.5	**5b**	25
4b	CN^-	95% DMF	20	3	**6b**	39
3a	MeO^-	DMF	20	2	**5c**	54
3b	MeO^-	DMF	20	2	**5c**	59
3a	OH^-[a]	95% DMF	20	4	**5d**	60
3b	OH^-[a]	95% DMF	20	4	**5d**	63
3a	OH^-[b]	95% DMF	20	4	**5d**	89
3b	OH^-[b]	95% DMF	20	4	**5d**	91
3a	$PhNH_2$		90	10	**5e**	80
3b	$PhNH_2$		20	10	**5e**	89
3a	AcO^-[c]	95% AcOH	65	5	**5f**	20
3b	AcO^-[c]	95% AcOH	65	5	**5f**	30
3b	AcO^-[c]	95% DMF	20	4	**5g**	95

[a] Base; NaOH. [b] Base, AcONa. [c] Reaction was carried out in the presence of $PdCl_2$.

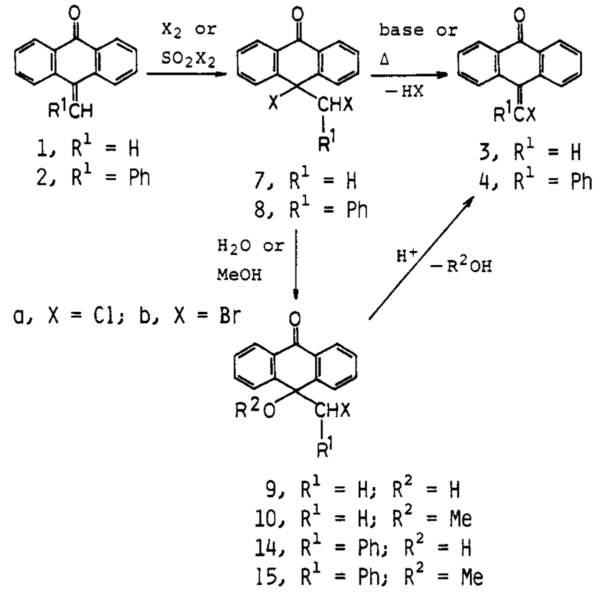
anthrones 3–6 which might be used as a starting material in synthesis.

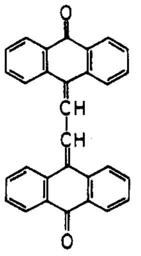
Results and Discussion

Preparation of 10-(Halomethylene)anthrones. The (halomethylene)anthrones **3** were prepared by the path as shown in Scheme I. The addition of halogen to the double bond of 10-methyleneanthrone (**1**) forms the dihalides **7**, and solvolysis of **7** gives **9** and **10**, the dehydrolysis and the demethanolysis of which produces **3**. The dichloride **7a** and the dibromide **7b** were prepared by the reaction of **1** with sulfuryl chloride and by bromine addition of **1** according to literature,[5] respectively. The solvolysis reaction (i.e., hydrolysis and methanolysis) of **7a,b** occurred in the halogeno group of 10-position, yielding the corresponding 10-hydroxy- and 10-methoxy-10-(halomethyl)anthrones **9** and **10** (**9a**, 66%; **9b**, 82%; **10a**, 57%; **10b**, 72%). The predominant replacement at the 10-position is compatible with common observation that tertiary halides are more reactive than primary halides in solvolysis reactions. The dehydrolysis of **9a** and the demethanolysis of **10a** with sulfuric acid gave 10-(chloromethylene)anthrone (**3a**) in 92% and 87% yields, respectively. Similar reactions of **9b** and **10b** led to the bromo analogue **3b** in 85–90% yields. Attempts of the dehydrohalogenation of dihalides **7a,b** with base, such as sodium hydroxide or sodium methoxide, gave **1** and its Diels–Alder dimeric product, 2,3-dihydrospiro[benz[*de*]anthrone-3,10′-anthrone] (**11**), which was formed by base-induced reaction of **1**. Thermolysis of **9a** in refluxing acetic acid led to **3a**, **11**, and **12**; however, **9b** gave 10,10′-(1,2-ethanediylidene)dianthrone (**13**).

10-(α-Chlorobenzylidene)anthrone (**4a**) was prepared, albeit in 15% yield, only by thermolysis of the dichloride **8a**, which was obtained from the reaction of 10-benzylideneanthrone (**2**) with sulfuryl chloride. The α-bromo analogue **4b** was obtained in a 87% yield from base-induced dehydrobromination of the dibromide **8b**, prepared according to the literature,[6] with sodium ethoxide at 15 °C. This base-induced dehydrobromination was accompanied by a debromination to **2** when the reaction temperature was raised; at a temperature above 30 °C, the debromination became the main reaction. A number of unsuccessful preparations by the routes that involve solvolysis of **8** to form **14** and **15** followed by dehydrolysis or demethanolysis to **4** and base-induced dehydrochlorination of **8a** to **4a** were attempted. The (halomethylene)anthrones **3** and **4** were stable, and their prolonged heating in an inert solvent only resulted in the formation of traces of anthraquinone.

Scheme I





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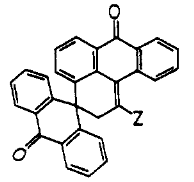

11, Z = H
12, Z = Cl

Vinylic Substitution of 10-(Halomethylene)anthrones. The (halomethylene)anthrones **3** and **4** reacted with nucleophiles, yielding the corresponding α-substituted 10-methyleneanthrones **5** and **6** or their subsequent products, as shown in Table I and Scheme II. Treatment of **3a,b** with sodium azide in *N,N*-dimethylformamide (DMF) gave 10-(azidomethylene)anthrone (**5a**), whose structure was substantiated by the infrared spectrum supporting the presence of azido group (2105 cm^{-1}) and its chemical behavior. The compound **5a** was stable

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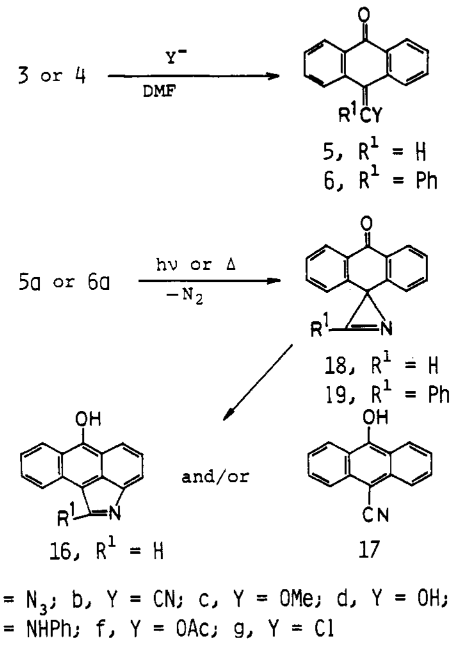
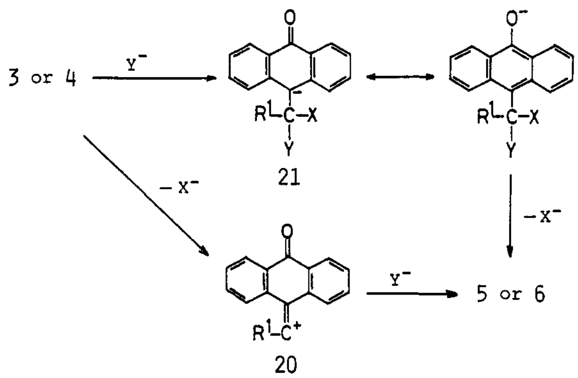
Scheme II



at 0 °C for periods up to 20 days; however, at 30 °C, it was transformed to 6-hydroxy-2-azaaceanthrylene (**16**) (38%) and anthraquinone. Photolysis of **5a** in ether at −50 °C afforded **16** (32%) and 9-hydroxy-10-cyanoanthracene (**17**) (16%) which arose from the secondary reaction of an intermediate spiro[anthrone-10,2′-2′*H*-azirine] (**18**). The formation of **18** was supported by NMR analysis of the crude photolysate which showed the presence of 2′-H of **18** [δ 9.68 (s)]. The spiroazirine **18**, which lacks a substituent at the 2′-position, could not be isolated owing to its extreme reactivity.[7] 10-(α-Bromobenzylidene)anthrone (**4b**) reacted with azide ion to give 3-phenylspiro[anthrone-10,2′-2′*H*-azirine] (**19**). This reaction probably involves the initial formation of **6a**, followed by its thermolysis.[8] The spectral data of **19** were consistent with the proposed structure.

The reaction of **3a** (**3b**) with potassium cyanide, buffered by acetic acid, in 95 vol % DMF yielded 10-(cyanomethylene)anthrone (**5b**) together with unidentified product whose oxidation by atmospheric oxygen to form anthraquinone. The spectra of **5b** indicated absorption for cyano and carbonyl groups at 2200 and 1653 cm^{-1}, respectively, and a singlet methine signal at δ 6.16. The similar reaction of **4b** gave 10-(α-cyanobenzylidene)anthrone (**6b**), which showed strong cyano and carbonyl absorptions (2200 and 1675 cm^{-1}). Treatment of **3a** (**3b**) with sodium methoxide in DMF, sodium hydroxide (or hydroxide ion provided by the ionization of sodium acetate) in 95 vol % DMF, and aniline led to 10-(methoxymethylene)anthrone (**5c**) and the hydroxy and anilino analogues **5d** and **5e**, respectively. On the other hand, **4b** was unreactive to these nucleophiles. The structure of product obtained from the reaction with aniline is assigned as enamine form **5e** rather than its imino form on the basis that its NMR spectrum reveals a broad singlet NH signal at δ 3.15 and its infrared spectrum indicates absorption for NH group at 3420 cm^{-1}.

Scheme III



For such nucleophilic substitution of halogeno group at (halomethylene)anthrones **3a**, **3b**, and **4b**, two mechanisms (the nucleophilic addition–elimination route, Ad$_N$-E, and S$_N$1 route) are conceivable (Scheme III).[4,8,9] However, it seems unlikely that the substitution reaction proceess by S$_N$1 route.[4,8-10] This view is supported by the following observations: (a) the (halomethylene)anthrones react with good nucleophiles to give the substitution products but do not react with poor nucleophiles such as acetate and chloride; (b) (bromomethylene)anthrone **3b** is more reactive than (α-bromobenzylidene)anthrone **4b**; (c) the substitution reactions proceed rapidly at ordinary temperature. If the S$_N$1 route is operative, the reaction would be not influenced by the nature of the attacking nucleophile, since the combination of vinyl cation **20** with nucleophiles generally occurs very fast. In addition, **3b** would be less reactive than **4b**, having phenyl group at the bromo-bearing carbon, which forms an intermediate vinyl cation stabilized due to Π(α-Ar)–p(C$^+$) conjugation.[4] The solvolysis of 10-(α-bromoarylidene)anthrones via S$_N$1 route involving the formation of vinyl cation has been reported to generally occur at a high reaction temperature.[4] Therefore, it seems reasonable that the vinylic substitution of **3a**, **3b**, and **4b** proceeds by Ad$_N$-E route, which involves the attack of a nucleophile on α-carbon atoms to form carbanion **21** with subsequent elimination of halide ion. The intermediate carbanion **21** may be stabilized by resonance and an inductive electron-withdrawing effect of carbonyl group.

On the other hand, (halomethylene)anthrones reacted with poor nucleophiles in the presence of palladium chloride. The palladium catalytic reaction of **3a** (**3b**) with sodium acetate in acetic acid gave the α-acetoxy analogue **5f**, albeit in a low yield. The structure of **5f** was confirmed by comparison with a sample prepared independently by acetylation of **5d** with acetic anhydride. A similar reaction of **3b** with sodium chloride in 95 vol % DMF led to **5g** (=**3a**) in a high yield. This palladium catalytic reaction would proceed by the mechanism similar to that proposed for the acetoxylation of vinyl halides, and would involve the formation of the intermediate **22**.[11]

Finally, the α-substituted 10-methylene- and 10-benzylideneanthrones **3**–**6**, except **5a**, are stable enough to subject to a further series of experiments.

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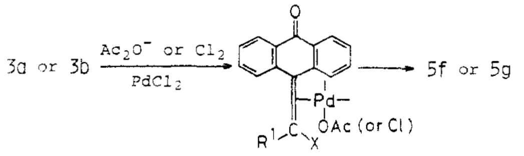

22

Experimental Section

Melting points were determined with a Yanagimoto hot stage apparatus and are uncorrected. Microanalysis were performed on a Perkin-Elmer Model 240 elemental analyzer. Infrared spectra were recorded on a JASCO IRA-1 spectrophotometer (KBr disk), ^{1}H NMR spectra on a JEOL JNM-3H-60 (60 MHz) and JNM-FX90 (90 MHz) spectometers for solutions in deuteriochloroform (tetramethylsilane as the standard), and mass spectra on a JEOL JMS-01SG-2 spectrometer (at 75 eV). Column chromatography was carried out with Wakogel C-200. Purity of products was checked by TLC (Merck, silica gel 60 F_{254}, precoated plastic sheet, 0.2 mm) and spectral analyses.

The following compounds were prepared according to previously known procedure: 10-methyleneanthrone (**1**),[12] 10-benzylideneanthrone (**2**),[2a] 10-bromo-10-bromomethylanthrone (**7b**),[5] and 10-bromo-10-(α-bromobenzyl)anthrone (**8b**).[6]

10-Chloro-10-(chloromethyl)anthrone (7a). To a stirred solution of **1** (4.12 g, 20 mmol) in methylenechloride (40 mL) was added sulfuryl chloride (8.10 g, 60 mmol) in small portions at room temperature. After 3 h, the solvent and unchanged sulfuryl chloride were distilled off under reduced pressure. The residue was recrystallized from benzene–hexane to give **7a** (4.15 g, 75%) as colorless plates: mp 156 °C; IR 1662 cm^{-1} (C=O); ^{1}H NMR δ 4.30 (s, 2 H, CH$_2$), 7.20–8.10 (m, 6 H, Ar H), 8.15–8.45 (m, 2 H, Ar H); MS, *m/e* 280/278/276 (M$^+$). Anal. Calcd for $C_{15}H_{10}Cl_2O$: C, 65.01; H, 3.65; Cl, 25.58. Found: C, 64.79; H, 3.61; Cl, 25.43.

10-Chloro-10-(α-chlorobenzyl)anthrone (8a). The procedure was similar to that for the preparation of **7a**. The product from **2** was recrystallized from benzene–hexane, giving **8a** (86%) as colorless microcrystals: mp 155–156 °C.

10-(Chloromethyl)-10-hydroxyanthrone (9a). A solution of **7a** (2.77 g, 10 mmol) in 80 vol % acetone (100 mL) was refluxed until TLC showed the absence of **7a** (3 h). The resulting solution was concentrated to one-third of its original volume and then was poured into water (200 mL). The precipitate was recrystallized from benzene–hexane to give **9a** (1.70 g, 66%) as colorless plates: mp 161 °C; IR 3440 (OH), 1655 cm^{-1} (C=O); ^{1}H NMR δ 3.64 (s, 1 H, OH), 3.70 (s, 2 H, CH$_2$), 7.25–8.25 (m, 8 H, Ar H); MS, *m/e* 260/258 (M$^+$). Anal. Calcd for $C_{15}H_{11}ClO_2$: C, 69.66; H, 4.29; Cl, 13.70. Found: C, 69.51; H, 4.35; Cl, 13.88.

10-(Bromomethyl)-10-hydroxyanthrone (9b). The procedure was similar to that the preparation of **9a**. The product was recrystallized to give **9b** (82%) as yellowish plates: mp 170–172 °C.

10-(Chloromethyl)-10-methoxyanthrone (10a). A solution of **7a** (2.77 g, 10 mmol) in methanol (50 mL) was heated under reflux for 15 h, during which time TLC showed the absence of **7a**. The solvent was distilled off, and the residue was chromatographed on silica (benzene as eluant). The first fraction was recrystallized from benzene–hexane to give **10a** (1.56 g, 57%) as colorless plates: mp 111–112 °C; IR 1655 cm^{-1} (C=O); ^{1}H NMR δ 2.99 (s, 3 H, CH$_3$), 3.75 (s, 2 H, CH$_2$), 7.35–7.95 (m, 6 H, Ar H), 8.20–8.55 (m, 2 H, Ar H); MS, *m/e* 274/272 (M$^+$). Anal. Calcd for $C_{16}H_{13}ClO_2$: C, 70.48; H, 4.80; Cl, 13.00. Found: C, 70.25; H, 4.71; Cl, 12.99.

10-(Bromomethyl)-10-methoxyanthrone (10b). A similar methanolysis of **7b** gave **10b** (72%): yellowish microcrystals (from methanol), mp 113–115 °C.

10-(α-Bromobenzyl)-10-methoxyanthrone (15b). The product from methanolysis of **8b** was recrystallized from methanol to give **15b** (79%) as colorless plates: mp 158–160 °C.

10-(Chloromethylene)anthrone (3a). A. Dehydrolysis of 9a. A solution of **9a** (2.59 g, 10 mmol) in sulfuric acid (20 mL) was allowed to stand at room temperature for 30 min. The resulting mixture was poured into ice water (200 g), and the precipitate was collected and washed with water. Recrystallization from benzene–hexane gave **3a** (2.21 g, 92%) as colorless plates, mp 133–134 °C (lit.[2c] mp 134 °C), identical with an authentic specimen.

B. Demethanolysis of 10a. A similar treatment of **10a** with sulfuric acid gave **3a** in a 87% yield.

C. Thermolysis of 7a. A solution of **7a** (2.59 g, 10 mmol) in acetic acid (50 mL) was refluxed under nitrogen until TLC showed the absence of the starting material (ca. 15 h). The resulting mixture was poured into water, and the precipitate was chromatographed on silica (benzene as eluant). The first eluate contained **3a** (0.41 g, 17%). The second fraction consisted of 1-chloro-2,3-dihydrospiro[benz[*de*]anthrone-3,10′-anthrone] (**12**) (0.48 g, 22%): white microcrystals (from benzene–hexane), mp 252 °C. The third fraction afforded 2,3-dihydrospiro[benz[*de*]-anthrone-3,10′-anthrone] (**11**) (0.31 g, 15%), identical with an authentic specimen.[3c]

10-(Bromomethylene)anthrone (3b). The compound **3b** was prepared in 85–90% yields both by dehydrolysis of **9b** and by demethanolysis of **10b**. The procedure was similar to that for the preparation of **3a**. **3b**: light yellow microcrystals (from benzene–hexane), mp 130 °C; IR 1660 cm^{-1} (C=O); ^{1}H NMR δ 7.25 (s, 1 H, CH), 7.25–7.85 (m, 5 H, Ar H), 8.05–8.65 (m, 3 H, Ar H); MS, *m/e* 286/284 (M$^+$). Anal. Calcd for $C_{15}H_9BrO$: C, 63.21; H, 3.18; Br, 28.03. Found: C, 63.10; H, 3.25; Br, 28.46.

Thermolysis of **7b** (3.66 g, 10 mmol) in refluxing acetic acid (50 mL) gave 10,10′-(1,2-ethanediylidene)dianthrone (**13**) (1.25 g, 61%) as orange-red microcrystals, mp 290 °C (lit.[2g] mp 292–294 °C), identical with an authentic specimen.

10-(α-Chlorobenzylidene)anthrone (4a). Themolysis of **8a** (1.77 g, 5 mmol) in refluxing acetic acid (60 mL) gave **4a** (0.47 g, 15%): yellow microcrystals (from benzene–hexane), mp 135–136 °C (lit.[13] mp 134–136 °C). Treatment of **8a** with strong bases did not yield **4a**.

10-(α-Bromobenzylidene)anthrone (4b). A solution of **8b** (4.42 g, 10 mmol) and sodium ethoxide (0.11 mol) in ethanol (200 mL) was stirred at 15 °C under nitrogen for 5 h. The solvent was evaporated, and then the resulting mixture was poured into water. The precipitate was recrystallized from benzene–hexane to give **4b** (3.14 g, 87%) as light yellow needles, mp 145 °C (lit.[4c,d] mp 147 °C), identical with an authentic specimen. Demethanolysis of **15b** with sulfuric acid were unsuccessful .

10-(Azidomethylene)anthrone (5a). Sodium azide (0.81 g, 12.5 mmol) was added to a solution of **3a** (1.20 g, 5 mmol) of *N,N*-dimethylformamide (DMF, 30 mL). The resulting mixture was stirred at 0 °C for 30 min and then poured into ice-water. The yellow precipitate was filtered off, washed with cold water, and dried at the temperature below 0 °C. Crude **5a** weighed 2.32 g (94%). Owing to its instability, it was examined without further treatment: mp 114–116 °C dec; IR 2105 (N$_3$), 1635 cm^{-1} (C=O); ^{1}H NMR δ 7.43 (s, 1 H, CH), 7.20–7.80 (m, 5 H, Ar H), 8.15–8.60 (m, 3 H, Ar H); MS, *m/e* 219 (M$^+$ – N$_2$). Anal. Calcd for $C_{15}H_9N_3O$: C, 72.86; H, 3.67; N, 17.00. Found: C, 72.53; H, 3.87; N, 16.72.

A similar reaction of **3b** with sodium azide also yielded **5a** (92%).

Photolysis of 5a. A solution of **5a** (0.50 g, 2 mmol) in ether (300 mL) under nitrogen was irradiated through a Pyrex filter with a 100-W high-pressure mercury lamp (Ushio UM102) for 1.5 h at –50 °C. The solvent was removed under reduced pressure. TLC (chloroform) of the crude photolysate showed two major spots having R_f 0.15 and 0.10 and a minor spot having R_f 0.35. The product was chromatographed on silica with chloroform. The first eluate contained 9-hydroxy-10-cyanoanthracene (**17**) (70 mg, 16%): light yellow needles (from chloroform), mp 272–273 °C; R_f 0.15; IR 3250 (OH), 2240 cm^{-1} (CN); ^{1}H NMR [CDCl$_3$–(CD$_3$)$_2$CO] δ 7.30–7.85 (m, 4 H, 2-, 3-, 6-, and 7-H), 8.20–8.65 (m, 4 H, 1-, 4-, 5-, and 8-H), 10.06 (s, 1 H, exchanged in D$_2$O, OH); MS, *m/e* (relative intensity) 219 (M$^+$, 100), 190 (90), 164 (27), 163 (27). Anal. Calcd for $C_{15}H_9NO$: C, 82.19; H, 4.14; N, 6.39. Found: C, 82.17; H, 3.98; N, 6.27. The second fraction consisted of 6-hydroxy-2-azaaceanthrylene (**16**) (0.14 g, 32%): light yellow

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column (from chloroform), mp 275–276 °C; R_f 0.10; IR 3200 (OH), 1638 cm^{-1} (C=N); ^{1}H NMR [$CDCl_3$–$(CD_3)_2CO$] δ 7.15–8.20 (m, 8 H, 1-H and Ar H), 10.42 (br s, 1 H, exchanged in D_2O, OH); MS, *m/e* (relative intensity) 219 (M^+, 100), 190 (28), 164 (77), 163 (71). Anal. Calcd for $C_{15}H_9NO$: C, 82.19; H, 4.14; N, 6.39. Found: C, 82.05; H, 3.96; N, 6.21. The compound having R_f 0.35 could not isolated owing to its extreme reactivity.

3-Phenylspiro[anthrone-10,2′-2′*H*-azirine] (19). (Bromobenzylidene)anthrone **4b** was allowed to react with sodium azide at 20 °C as described above for the reaction of **3** with sodium azide. The product was recrystallized from benzene–hexane to give **19** (90%) as light yellow plates: mp 194 °C dec; IR 1750 (C=N), 1660 cm^{-1} (C=O); ^{1}H NMR δ 6.90–7.30 (m, 2 H, 4- and 5-H), 7.30–8.05 (m, 9 H, 2-, 3-, 6-, and 7-H and C_6H_5), 8.35–8.70 (m, 2 H, 1- and 8-H); MS, *m/e* (relative intensity) 295 (M^+, 100), 192 (20), 164 (68), 163 (46). Anal. Calcd for $C_{21}H_{13}NO$: C, 85.40; H, 4.44; N, 4.74. Found: C, 85.23; H, 4.59; N, 4.91. Treatment of **4b** with sodium azide at 0 °C gave the unchanged starting material.

10-(Cyanomethylene)anthrone (5b). A suspension of potassium cyanide (0.81 g, 12.5 mmol) in water (1 mL) added to a stirred solution of **3a** (1.20 g, 5 mmol) in DMF (19 mL) and acetic acid (0.5 mL). The resulting soltuion was stirred at 20 °C under nitrogen for 30 min. The mixture was poured into water, and the precipitate which had separated was collected. The product was chromatographed on silica (benzene as eluant). The first fraction afforded anthraquinone (52 mg, 5%). The second fraction contained **5b** (0.23 g, 20%): colorless microcrystals (from benzene–hexane), mp 198 °C; IR 2200 (CN), 1653 cm^{-1} (C=O); ^{1}H NMR δ 6.16 (s, 1 H, CH), 7.45–7.90 (m, 5 H, 2-, 3-, 5-, 6-, and 7-H), 8.20–8.45 (m, 2 H, 1- and 8-H), 8.45–8.65 (m, 1 H, 4-H), MS, *m/e* (relative intensity) 231 (M^+, 100), 203 (60), 202 (14), 201 (12), 88 (11). Anal. Calcd for $C_{16}H_9NO$: C, 83.10; H, 3.92; N, 6.06. Found: C, 83.08; H, 4.04; N, 6.02. A similar treatment of **3b** gave **5b** in a 25% yield.

10-(α-Cyanobenzylidene)anthrone (6b). To a stirred solution of **4b** (1.08 g, 3 mmol) in DMF (19 mL) was added a suspension of potassium cyanide (0.48 g, 7.5 mmol) in water (1 mL). After 3 h, the resulting mixture was poured into water. Chromatography (benzene as eluant) of product gave anthraquinone (25 mg, 4%) and **6b** (0.35 g, 39%): pale yellow microcrystals (from benzene–hexane), mp 191–192 °C.

10-(Methoxymethylene)anthrone (5c). To a mixture of sodium methoxide (0.68 g, 12.5 mmol) in DMF or methanol (15 mL), **3a** (1.20 g, 5 mmol) was added in small portions. The resulting mixture was stirred under nitrogen for 2 h, poured into water, and acidified with hydrochloric acid. The crystals were filtered off, and then chromtographed on silica with benzene to give anthraquinone and **5c** (0.63 g, 54%), mp 138 °C (lit.[2c] mp 136 °C), identical with an authentic specimen. Similar treatment of **3b** gave **5c** (59%).

10-(Hydroxymethylene)anthrone (5d). A suspension of sodium acetate (1.03 g, 12.5 mmol) in water (1.5 mL) was added to a stirred solution of **3a** (1.20 g, 5 mmol) in DMF (28.5 mL) under nitrogen. After 4 h (20 °C), the mixture was poured into water. The product **5d** (0.99 g, 89%) was isolated as orange microcrystals, identical (IR spectrum) with an authentic specimen prepared by isomerization of spiro[anthrone-10,2′-oxirane] with boron trifluoride etherate.[2b–d] Similar treatment of **3b** afforded in a 91% yield. The reaction of **3a,b** in the presence of sodium hydroxide, followed by acidification, gave **5d** in 60–63% yields.

10-(Anilinomethylene)anthrone (5e). A mixture of **3b** (1.43 g, 5 mmol) and aniline (4 mL) was stirred at 20 °C for 10 h. Removal of the excess aniline by steam distillation gave red crystals, which were recrystallized from benzene–hexane to yield **5e** (1.32 g, 89%) as red microcrystals, identical with an authentic specimen, mp 210–212 °C (lit.[2c] mp 205 °C). Similar treatment of **3a** with aniline at 60 °C also gave **5e** (80%).

10-(Acetoxymethylene)anthrone (5f). To a suspension of **3a** (1.20 g, 5 mmol) and palladium chloride (0.18 g, 1 mmol) in acetic acid (18 mL) was added a suspension of sodium acetate (1.03 g, 12.5 mmol) in water (2 mL). The resulting mixture was stirred under nitogen at 65 °C for 5 h and then poured into water. The product was chromatographed on silica (benzene as eluant). The first eluate contained unchanged **3a** (0.21 g, 18%). The second fraction consisted of anthraquinone (70 mg, 7%), and the third fraction gave **5f** (0.26 g, 20%): light yellow microcrystals (from benzene–hexane), mp 153–154 °C; IR 1782 (C=O), 1665 cm^{-1} (C=O); ^{1}H NMR δ 2.38 (s, 3 H, CH_3), 7.35–8.00 (m, 5 H, CH and 2-, 3-, and 6-, and 7-H), 8.20–8.55 (m, 4 H, 1-, 4-, 5-, and 8-H); MS, *m/e* (relative intensity) 264 (M^+, 18), 222 (100), 221 (30), 194 (26), 165 (31), 43 (29). Anal. Calcd for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.07; H, 4.53.

The compound **5f** was prepared independently by the following experiment. **5d** (1.11 g, 5 mmol) was suspended in acetic anhydride (10 mL), and then sodium acetate (0.5 g) was added. The mixture was heated at 90 °C for 2 h and then poured into water. The product was recrystallized from benzene–hexane to give **6f** (1.10 g, 83%).

Registry No. **1**, 4159-04-0; **2**, 14343-92-1; **3a**, 100606-11-9; **3b**, 100606-12-0; **4a**, 100606-13-1; **4b**, 74975-68-1; **5a**, 100606-14-2; **5b**, 21745-70-0; **5c**, 100655-51-4; **5d**, 70450-65-6; **5e**, 70450-86-1; **5f**, 100606-15-3; **6b**, 100606-17-5; **7a**, 100606-16-4; **7b**, 72423-87-1; **8a**, 100606-18-6; **8b**, 74975-71-6; **9a**, 100606-19-7; **9b**, 100606-20-0; **10a**, 100606-21-1; **10b**, 100606-22-2; **11**, 100606-23-3; **12**, 100606-24-4; **13**, 5816-02-4; **15b**, 100606-25-5; **16**, 100606-26-6; **17**, 14789-46-9; **19**, 100606-27-7; anthraquinone, 84-65-1.

Supplementary Material Available: Characterization data of **5e**, **6b**, **8a**, **9b**, **10b**, **12**, **14b**, and **15b** (2 pages). Ordering information is given on any current masthead page.